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BLEACHABILITY OF KRAFT PULPS TREATED BY ETHANOL-BASED CHLORINE DIOXIDE DELIGNIFICATION SEQUENCES

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ABSTRACT

Kraft pulps delignified with ethanol-based chlorine dioxide (D_0) stages yielded pulps with higher brightness levels than aqueous D_0 stages. However, when these pulps were subjected to aqueous extraction (E) stage, the ethanol D_0 pulps were more difficult to brighten with a second chlorine dioxide (D_1) stage than were aqueous D_0 pulps. The pulps from a combination of ethanol D_0 and acid ethanol extraction (A_E) stages were also more difficult to brighten than aqueous D_0E pulps. An A_E stage was less efficient and less selective at removing lignin than an aqueous caustic extraction. Apparently, chromophores are developed in ethanol-based D_0 and A_E stages that negatively impact D_1 bleachability.

INTRODUCTION

Alternatives to conventional kraft pulping and chlorine-based bleaching are being sought to produce strong pulps while minimizing the impact on the environment. Pulping processes that employ ethanol-water solvents would reduce fresh water consumption and possibly eliminate the production of malodorous sulfur compounds during pulping.[2-4] Recently, the application of ethanol-water solutions in ozone bleaching has been evaluated by several investigators[5,6] as a method for increasing ozone bleaching selectivity.

Our studies have examined the use of ethanol-water bleaching media in the first chlorine dioxide delignification (D_0) stage[7] and in the first extraction stage.[7-11] Considerable amounts of lignin can be removed from D_0-treated pulps by an acid ethanol extraction stage (A_E).[10] An appealing aspect of the A_E stage is that an ethanol-based partial bleaching sequence could be developed that does not require alternating between acidic and alkaline stages. The effluents from the stages could be combined and evaporated to recover the ethanol and possibly a commercially valuable oxidized lignin. Furthermore, the D_0 stage effluent, after pH adjustment, could possibly be used in the A_E stage, allowing the two to be combined in a (D_0/A_E) stage. This would reduce the amount of ethanol needed and increase the economic viability of the D_0A_E sequence.

In this paper, we examine how the A_E medium (i.e., D_0 effluent or fresh ethanol-water solution) influences A_E stage delignification. Comparisons are made between an optimized D_0A_E and aqueous D_0E sequence in terms of delignification, incremental brightness development, and D_1 bleachability. Also, in this report, we examine the impact of the D_0 stage bleaching medium on D_1 bleachability.

RESULTS AND DISCUSSION

Initial D_0A_E and (D_0/A_E) Bleaching Results

Several small-scale experiments were performed to ascertain the optimum conditions for delignification and selectivity for the ethanol-based D_0A_E sequence. Most of the initial conditions chosen for the A_E stage were based on our previous study.[10] Approximately 50% of the residual lignin was removed with the D_0A_E sequence (Table 1). The bulk of this delignification (~35%) occurred within the D_0 stage. Two interesting observations were made with this sequence. First, the brightness of the pulp decreased by 8 to 10 points across the A_E stage, and second, the A_E stage pH decreased from 4.2 to 3.5. This pH drop was not observed in our earlier study,[10] probably because the consistency used in that study (1.25%) was lower than in the present one (3.0%).

TABLE 1
Initial Results from Ethanol-Based D_0A_E and (D_0/A_E) Partial Sequences.

	A_E Stage Reaction Time (hrs.)	Kappa Number	Residual Lignin (%)	ISO Brightness (%)
Unbleached	-	30.1	4.63	19.7
D_0	-	13.2	3.02	34.5
D_0A_E	2.5	9.3	2.18	24.0
D_0A_E	5.0	9.4	2.27	26.0
(D_0/A_E)	1.0	9.6	2.18	27.1
(D_0/A_E)	2.5	7.8	1.78	29.0
(D_0/A_E)	5.0	7.2	1.83	27.5

Effect of A_E Stage pH on Delignification

A second series of experiments employed the D_0 stage effluent as the ethanol-water medium in the A_E stage (Table 1). Such a bleaching sequence has no interstage washing and was denoted as (D_0/A_E). Surprisingly, the (D_0/A_E) sequence was more efficient at delignification than the D_0A_E. This enhancement could be caused by the reaction of trace amounts of chlorite (ClO_2^-) in the extraction medium. The bulk of the lignin removal with an A_E stage occurred within the first 2.5 hours of extraction. The pulp brightness and pH decreased during the A_E stage of the (D_0/A_E); a similar decrease was observed in the D_0A_E sequence.

Increasing the initial A_E pH from 4.2 to 5.8 was detrimental for lignin extraction (Table 2). The poorer A_E delignification, particularly for the D_0A_E sequence, was likely related to the conversion of the carboxylic acids in the oxidized lignin to their sodium salts. A previous study[9] indicated that oxidized lignin has a lower *alkali* solubility in ethanol-water media than in water. Almost all of the increase in pulp brightness with the D_0 stage was lost when the A_E stage was operated at the higher pH levels.

Furthermore, with the high-pH A_E stage of the (D_0/A_E) sequence, there appeared to be some lignin condensation reactions, as evidenced by the increases in kappa number and residual lignin. Such increases could be related to condensation

TABLE 2
Effect of A_E Exit pH on D_0A_E and (D_0/A_E) Bleaching (5-Hr. A_E stage).

EtOH-Based Sequence	A_E Stage pH Initial	A_E Stage pH Final	Kappa Number	Residual Lignin (%)	ISO Brightness (%)
Unbleached	-	-	30.1	4.63	19.7
D_0	-	-	13.2	3.02	34.5
D_0A_E	4.2	3.5	9.4	2.27	26.0
D_0A_E	5.8	5.1	11.9	2.60	20.0
(D_0/A_E)	4.2	3.5	7.2	1.83	27.5
(D_0/A_E)	5.8	4.8	15.3	3.20	16.8

reactions between dissolved oxidized lignin and the lignin in the fiber; Simson *et al.*[12] and Brage *et al.*[13] report that quinonoid structures can condense with themselves under mildly acidic reaction conditions.

Additional small-scale trials evaluated minor changes in the A_E-stage pH on (D_0/A_E) bleaching (Table 3). Adjusting the final A_E-stage pH from 3.5 to 4.1 gradually decreased the overall amount of residual lignin removed and the brightness level obtained with the (D_0/A_E) sequence. The increased delignification efficiency of the (D_0/A_E) sequence with lower A_E-stage pH is presumably related to trace amounts of ClO_2^- in the A_E medium. Several studies have noted the increased reactivity of ClO_2^- with various lignin model compounds as the pH of the medium is decreased from 4 to 3.[13-16]

An A_E stage was conducted with fresh ethanol that contained 0.20 m$\underline{M}$ of ClO_2^- (Table 3). This experiment was performed to ascertain if trace levels of ClO_2^- in the A_E medium improves delignification. The addition of ClO_2^- enhanced both lignin removal and brightness development of the D_0A_E sequence to comparable levels of the (D_0/A_E) sequence. Thus, it appears that the improved performance of the (D_0/A_E) sequence is related to trace levels of ClO_2^- in the A_E medium. We have found 0.2-0.3 m$\underline{M}$ ClO_2^- in ethanol-based D_0 stage effluents.[7]

TABLE 3

Effects of pH and ClO_2^- in the A_E on D_0A_E and (D_0/A_E) Bleaching (2.5-Hr. A_E stage).

EtOH-Based Sequence	A_E Stage End pH	Kappa Number	Residual Lignin (%)	ISO Brightness (%)
Unbleached	-	30.1	4.63	19.7
(D_0/A_E)	4.1	9.3	2.12	34.5
(D_0/A_E)	3.9	8.3	2.00	25.4
(D_0/A_E)	3.6	8.1	1.91	26.3
(D_0/A_E)	3.4	7.8	1.78	29.0
D_0A_E (w/ 0.2 mM of ClO_2^- in A_E)	3.5	7.8	1.75	28.7
D_0A_E	3.6	9.3	2.18	24.0

Effect of (D_0/A_E) on Pulp Viscosity and Zero-Span Strength

The results of the previous section indicated that the optimum A_E exit pH for (D_0/A_E) delignification is ~3.5. However, acid hydrolysis of the glycosidic bonds in cellulose can become significant at pH levels below 4 when elevated temperatures are used (>100°C).[7,10] Indeed, the A_E stage significantly contributed to carbohydrate degradation and pulp strength loss as noted by pulp viscosity and zero-span breaking-length strength measurements (Table 4). The amount of pulp damage at the higher exit pH (3.9) was unexpected, based on our earlier observations.[10] One expects a 1 to 4 mPa•s decrease in pulp viscosity across an aqueous D_0E or $D_0(EO)$ sequence.[7,17,18] The (D_0/A_E) sequence was much more aggressive at carbohydrate degradation (~7 to 9 mPa•s decrease).

TABLE 4

Effect of Exit pH on (D_0/A_E) Carbohydrate Degradation (2.5-Hr. A_E stage).

	A_E Stage Exit pH	Viscosity (mPa•s)	Zero-Span Breaking Length Wet (km)	Dry (km)
Brownstock	-	25.1	16.0	20.8
D_0	-	24.5	16.2	21.0
(D_0/A_E)	3.5	16.4	6.7	12.7
(D_0/A_E)	3.9	18.6	10.0	16.2

Bleachability of (D_0/A_E)Versus Aqueous-Based D_0E Delignified Pulps

Large-scale runs of the ethanol-based (D_0/A_E) sequence were performed to produce enough pulp to conduct a D_1 bleachability trial (Table 5). These larger scale runs yielded pulps with higher kappa numbers, higher residual lignin values, and lower brightness levels than the corresponding small-scale (D_0/A_E) runs. The reason this occurred is unclear. The results from these large-scale (D_0/A_E) stages are almost comparable to the small-scale D_0A_E, possibly indicating that there was no residual ClO_2^- in the A_E medium.

TABLE 5
Comparison of the Ethanol-Based (D_0/A_E) and Aqueous D_0E Sequences.

Bleaching Sequence†	A_E stage Exit pH	Kappa Number	Residual Lignin (%)	ISO Brightness (%)	k_{457} (m^2/kg)
Aqueous D_0	-	16.6	2.98	32.9	4.8
Ethanol-based D_0	-	13.3	2.99	34.7	3.8
Aqueous D_0E	-	7.3	1.37	38.5	3.6
(D_0/A_E)	3.6	9.8	2.37	22.9	11.8
(D_0/A_E)	3.9	11.9	2.64	21.7	13.9
(D_0/A_E)E	3.6	8.7	1.51	29.2	7.9
(D_0/A_E)E	3.9	9.0	1.73	27.6	8.3

†All E stages performed with 100% aqueous medium; 2.5-hr. A_E stage.

The aqueous-based D_0E sequence was more efficient at lignin removal and brightness development than the (D_0/A_E) sequence. Nevertheless, an ethanol-based D_0 yielded a brighter pulp than its aqueous counterpart; this result agrees with our earlier observations[7] and will be discussed later in this report. Additional residual lignin was removed from the (D_0/A_E)-treated pulp using an aqueous E stage (Table 5, entries 6 & 7). However, the E-stage treatment did not increase the brightness or decrease the light absorption coefficient (k_{457}) to the post-D_0 values (34.7 ISO and 3.8 m^2/kg, respectively).

Some preliminary aqueous D_1 bleaching trials were conducted on the D_0E, (D_0/A_E), and (D_0/A_E)E pulps (Table 6). The D_1 stages performed directly on a (D_0/A_E)

TABLE 6
Brightness Development of Ethanol-Based (D_0/A_E)- and Aqueous D_0E-Treated Pulps with 1.25% ClO_2 in D_1 Stage.

Bleaching Sequence Prior to D_1 stage†	A_E stage Exit pH	ISO Brightness (%) Pre-D_1	Post-D_1
Aqueous D_0E	-	38.5	74.1
(D_0/A_E)	3.6	22.9	45.5
(D_0/A_E)	3.9	21.7	45.1
(D_0/A_E)E	3.6	29.2	69.2
(D_0/A_E)E	3.9	27.6	65.9

†All E stages performed with 100% aqueous medium; 2.5-hr. A_E stage.

pulp yielded a modest 23-point increase in brightness; an aqueous E-stage treatment of a (D_0/A_E) pulp, on the other hand, nearly doubled this incremental brightness gain across the D_1 stage. This result was not unexpected because the (D/A_E) pulps contained more extractable lignin, which consumed some of the applied ClO_2. The brightness of (D_0/A_E)ED_1 pulps were generally 5 to 10 points lower than D_0ED_1 pulps.

Several aqueous D_1 runs, at various applied ClO_2 levels, were performed on (D_0/A_E)E and aqueous D_0E pulps to obtain brightness response curves (Fig. 1). Both (D_0/A_E)E pulps afforded lower post-D_1 brightness levels than aqueous D_0E pulps at given amounts of ClO_2 consumed. The (D_0/A_E)E pulp at a 3.6 A_E exit pH generally required ~65% more ClO_2 to achieve a given D_1 brightness level than a D_0E pulp that had a similar amount of residual lignin.

The results in Figure 1 were fitted to a simple brightening model that has been used to characterize pulp bleachability:[19]

$$B = b_0 + b_1 \cdot \left(1 - e^{-b_2 x}\right) \quad (1)$$

where B is the predicted pulp brightness, x is the consumed amount of ClO_2, b_0 is the entering pulp brightness, and b_1 is the brightness gain across the D_1. The sum (b_0+b_1) represents the asymptotic brightness limit of the D_1 stage, and the last parameter, b_2, denotes the relative rate at which this asymptotic limit is approached.[19]

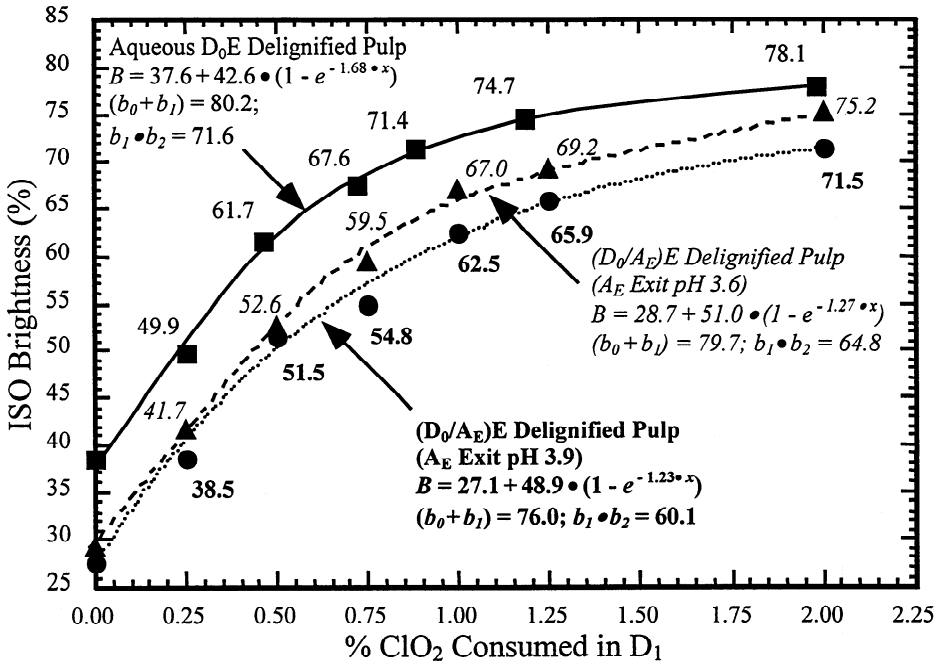

FIGURE 1. D_1-stage brightness response curves for $(D_0/A_E)E$- and D_0E-treated pulps (Table 6). Response curves are based on Eq. 1. An aqueous medium was used in all E and D_1 stages.

Equation 1 modeled the brightening response data well (R^2 >0.99) and quantitatively indicated the lower bleachability of $(D_0/A_E)E$ pulps (Fig. 1). The model predicts that $(D_0/A_E)E$ and D_0E pulps, which have similar residual lignin levels, will approach a common D_1 brightness ceiling of ~80 ISO, whereas the $(D_0/A_E)E$ pulp with the higher residual lignin will have a lower asymptotic limit (~76 ISO). The D_1 initial response factor, $b_1 \bullet b_2$, represents the initial slope of the brightness response curve (Eq. 1). A high $b_1 \bullet b_2$ value indicates a quick brightening response to a low level of consumed ClO_2.[19] The lower $b_1 \bullet b_2$ values for the $(D_0/A_E)E$ pulps clearly indicate the slower brightening response to ClO_2.

Possible Factors Affecting (D_0/A_E) Bleachability

The results of the D_1 bleachability study clearly established that (D_0/A_E) and $(D_0/A_E)E$ pulps are more difficult to brighten than aqueous-based D_0E pulps. Part

of the bleachability difference between the ethanol-based partial sequence and the conventional aqueous sequence is related to the A_E stage. The A_E stage is not as proficient or as selective at removing dissolvable lignin as an aqueous E stage; this lower delignification efficiency is presumably related to physico-chemical limiting factors.[7,9,11] In addition, the A_E stage increases the amount of chromophoric groups in the pulp, as is indicated by the higher value of k_{457} (Table 6). These k_{457} values after the A_E are close to the original k_{457} value of the unbleached pulp, although the (D_0/A_E) pulps have less residual lignin. These new chromophoric groups decrease pulp brightness, increase ClO_2 consumption, and, furthermore, may be more resistant to ClO_2 attack. At this time, it is unknown what types of chromophoric groups are produced during the A_E stage.

Another factor possibly influencing D_1 bleachability of (D_0/A_E) pulps is the previous D_0 stage. We have shown in an earlier study[20] that an ethanol-based D_0 stage yields an oxidized residual lignin that has more quinone structures than an aqueous D_0 stage. These structures could subsequently polymerize[12,13,21] in the A_E stage forming new structures, which result in a more difficult lignin to alkali extract and/or bleach in a D_1 stage.

Bleachability of Ethanol- Versus Aqueous-Based D_0 Delignified Pulps

The results from the previous section illustrated that the A_E stage is ineffective at lignin removal and negatively impacts future bleachability. However, looking back at the data from Table 5 on the various delignification sequences, we see that an ethanol-based D_0 stage provides a pulp that has 2 units higher brightness and slightly lower k_{457} than its aqueous counterpart. Apparently, the oxidized lignin in the ethanol-based D_0 pulps is less colored than the oxidized lignin in aqueous D_0 pulps.

Aqueous E stages performed on these pulps yielded some interesting results (Table 7). After extraction, the ethanol D_0 pulp had approximately the same kappa

TABLE 7

Effects of D_0 Bleaching Medium on Subsequent Aqueous E-Stage Brightness, Residual Lignin Removal, and Chromophore Reduction (i.e., k_{457}).

Type of Pulp	ISO Brightness (%)	Kappa Number	Residual Lignin (%)	Light Absorption Coeff. k_{457} (m^2/kg)
Unbleached Pulp	19.7	30.1	4.61	15.7
Aqueous D_0 Stage				
Pre-Caustic Extraction	32.4	16.2	2.98	4.8
Post-Caustic Extraction	37.9	7.3	1.37	3.6
Ethanol-based D_0 Stage				
Pre-Caustic Extraction	34.9	13.6	2.99	3.8
Post-Caustic Extraction	35.7	7.7	1.41	3.7

number and total residual lignin level as the aqueous D_0 pulp. However, the aqueous D_0 pulp had a higher brightness after extraction than the ethanol D_0 pulp. In addition, the brightness of the aqueous D_0 pulp increased 5 points during caustic extraction as compared to the brightness of the ethanol D_0 pulp, which increased by 1 point. There was little change in the k_{457} for the ethanol D_0 pulp after an aqueous E stage, whereas the k_{457} for the aqueous D_0 pulp decreased by ~25%.

The D_0E delignified pulps were subjected to aqueous D_1 stages to observe how the D_0 treatment impacts D_1 brightness. The D_1 brightness responses for these pulps, at various applied ClO_2 levels, are given in Figure 2. The pulps treated with an aqueous D_0 stage appeared easier to bleach with the D_1 stage, at a given ClO_2 charge, than pulps treated with an ethanol D_0, even though the two D_0E delignified pulps have approximately the same amount of residual lignin entering into the D_1 stage. Ethanol D_0 pulps consumed ~20% more ClO_2 to reach a given D_1 brightness level than the aqueous counterpart. Only trace ClO_2 residuals were detected in the D_1 effluents for ethanol D_0 pulps; aqueous D_0 pulps, on the other hand, were observed to have residuals up to 10% of applied ClO_2 charge in the D_1 effluents.

The data in Figure 2 were fitted to the simple brightening model (Eq. 1) to better characterized D_1 bleachability. Both D_0E pulps are predicted to reach a common D_1 brightness ceiling of ~80% ISO. The D_0 bleaching medium did not ap-

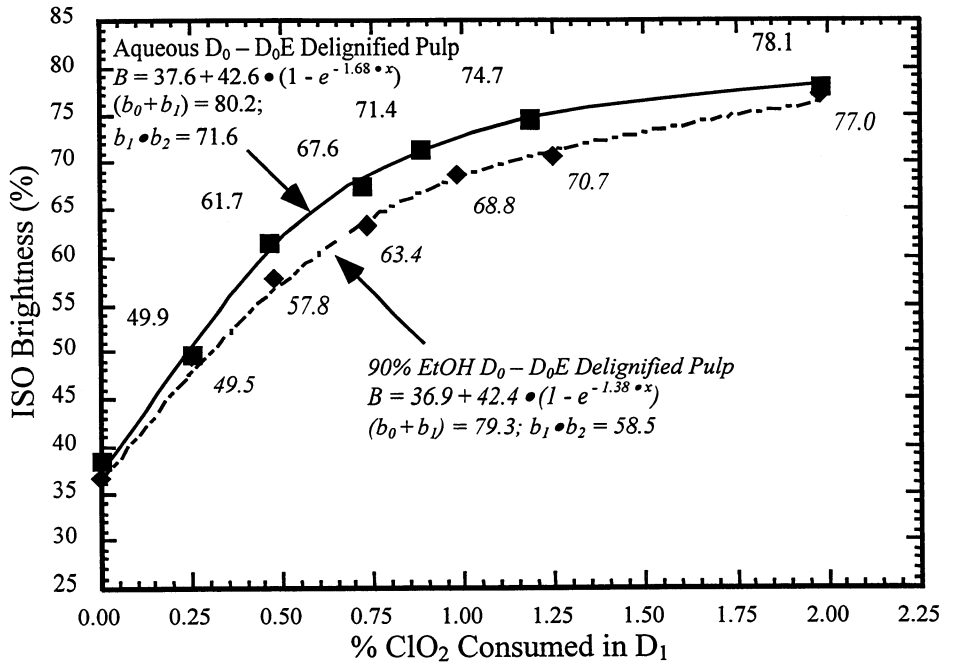

FIGURE 2. D_1-stage brightness response curves for D_0E-delignified pulps where either a 90% ethanol or an aqueous medium used in D_0 stage (Table 7). Response curves are based on Eq. 1. An aqueous medium was used in all E and D_1 stages.

pear to effect the maximum brightness gain (b_1) in the D_1 stage. However, the relative rate at which this brightness gain is approached is slower for the D_0 stage pulp bleached in an ethanol medium relative to an aqueous medium. As expected, the ethanol D_0 pulp had a lower $b_1 \bullet b_2$ value, suggesting that the remaining lignin is more difficult to brighten in a D_1 stage.

Possible Factors Affecting D_0E Bleachability

In addition to affecting the post-D_0 kappa number and brightness, the D_0 solvent had a significant influence on the subsequent E- and D_1-stage brightening response of the pulp. Our previous study, which examined D_0 stage delignification of ethanol- and aqueous-based systems, showed that residual lignin of ethanol D_0 pulps has more quinone structures than an aqueous-based D_0 stage.[20] The slow brightening response of ethanol D_0 pulps in the D_1 stage may be the result of addi-

tional quinone-type structures in the residual lignin. Brage *et al.*[13] have indicated that ClO_2 does not react with quinones to any appreciable extent; however, the authors point out that intermediate ClO_2^-, arising from other ClO_2 reactions, can react with quinones to afford oxidation products. These quinone structures are slowly eliminated during the D_1 when a sufficient amount of ClO_2^- has accumulated.

CONCLUSIONS

An ethanol-based (D_0/A_E) sequence using the D_0 effluent as the A_E medium generally showed improved delignification to that observed in the D_0A_E sequence. This improved delignification appeared to be related to the low concentrations of residual ClO_2^- from the D_0 effluent. The A_E stage is less efficient and selective at extracting dissolvable lignin than an aqueous E stage. Furthermore, the A_E stage generated additional chromophoric groups that persisted even after an aqueous E stage. Alkali extracted (D_0/A_E) pulps were more difficult to brighten in a D_1 stage than aqueous DE pulps. This lower D_1 bleachability of (D_0/A_E) delignified pulps is presumably related to changes in the residual lignin during both D_0 and A_E stages.

Ethanol-based D_0 stages yielded pulps with higher brightness levels than the aqueous controls. However, aqueous D_0 pulps were slightly brighter than the ethanol D_0 pulps after an aqueous caustic extraction stage. The extracted ethanol D_0 pulps were more difficult to brighten in a D_1 stage than the corresponding aqueous D_0E pulps. Presumably, the alterations in the residual lignin structure caused by an ethanol ClO_2 oxidation[7,20] adversely affects D_1 bleachability.

EXPERIMENTAL

Pulp Bleaching

A conventional kraft pulp (southern pine) was obtained from a mill and used throughout this study. Additional details about the pulping conditions are provided

in previous reports.[7,8] The pulp had a kappa number of 30.1 and a viscosity of 25.1 mPa•s. The D_0 stage was performed either with a 90% (v/v) ethanol or a 100% aqueous medium at the following conditions: 2.52% ClO_2 on o.d. pulp (0.22 kappa factor), 3% consistency, initial pH 4.2-4.6 prior to ClO_2 addition, 70°C, and 15-min. reaction time. The D_0 filtrate contained no significant residual ClO_2 and had an exit pH of 2.2 to 2.6.

Acid ethanol extractions (A_E stages) were performed on D_0 pulps bleached in a 90% ethanol medium. The extraction medium was either a fresh 90% ethanol solution or the previous D_0 effluent (i.e., (D_0/A_E) sequence). Sodium hydroxide or sodium acetate was added such that the A_E exit pH was ~3.4 to 4.2. All A_E stages were done at 3% consistency. Small- and large-scale A_E stages were performed in 300-mL and 2-L stirred Parr® bomb reactors, respectively, equipped with heating mantles and temperature controllers. Pulps were extracted for 2.5 hrs. (unless otherwise noted) at 130°C, cooled to ~65°C, and drained of extraction effluent to ~25% consistency. Afterwards, the pulp was washed first with 90% ethanol and later with copious amounts of deionized (DI) water. Technical grade $NaClO_2$ (~80% purity) was used in selected A_E-stage experiments.[7]

All E stages were performed with a 100% aqueous medium at the following conditions: 3.64% NaOH on o.d. pulp (0.55 caustic multiple), 10% consistency, 60°C, and 60-min. reaction time. All D_1 stages were performed with 100% aqueous medium under the following conditions: 10% consistency, 70°C, and 3-hr. reaction time. An amount of NaOH was added to the pulp, after the ClO_2 addition, such that the pulp slurry pH dropped to ~4.3 pH after 15 minutes of reaction. Generally, the D_1 effluent had an ending pH between 3.6 and 4.5. Both E and D_1 stages were conducted in Kapak®/Scotchpack sealable pouches. Residual ClO_2 in the D_1 effluent was determined idometrically.[7]

Analytical Measurements

Kappa numbers were determined by micro-kappa number measurements (TAPPI Useful Method UM-246). ISO brightness (TAPPI Standard T-525 om-92)

and dry zero-span breaking length (TAPPI Standard T-231 cm-85) measurements were made on selected treated pulps. Wet zero-span measurements were done by the above dry zero-span method except that the paper strips were briefly immersed in ultra-pure DI water and blotted dry prior to testing. Unused paper strips from the zero-span analyses were utilized for pulp viscosity measurements (TAPPI Standard T-230 om-89). Residual lignin was determined by the UV spectroscopic method described by Mallett[22] using a wavelength of 295 nm and lignin absorptivity value of 19.6 L/(g•cm).[7,20]

Light absorption coefficients at 457 nm (k_{457}) were measured on selected handsheets using a Technibrite™ Micro TB-1C brightness meter equipped with an opacity function. The basic guidelines of the measurement are given in TAPPI Standard T-425 om-91 and by Teder and Tormund.[23] All k_{457} values reported had corresponding light-scattering coefficients (s_{457}) of 24.6 to 28.0 m^2/kg.[7]

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